

UNCLASSIFIED

AD NUMBER	
AD324219	
CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	confidential
LIMITATION CHANGES	
TO:	Approved for public release, distribution unlimited
FROM:	Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JUL 1961. Other requests shall be referred to Office of Naval Research, Arlington, VA.
AUTHORITY	
15 Apr 1970, per doc markings; ONR ltr, 28 Aug 1968	

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 324219

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMEBON STATION ALEXANDRIA, VIRGINIA

CLASSIFICATION CHANGED
TO UNCLASSIFIED
FROM CONFIDENTIAL
PER AUTHORITY LISTED IN

TAB 70-8 DATED 15 APRIL 1970



UNCLASSIFIED

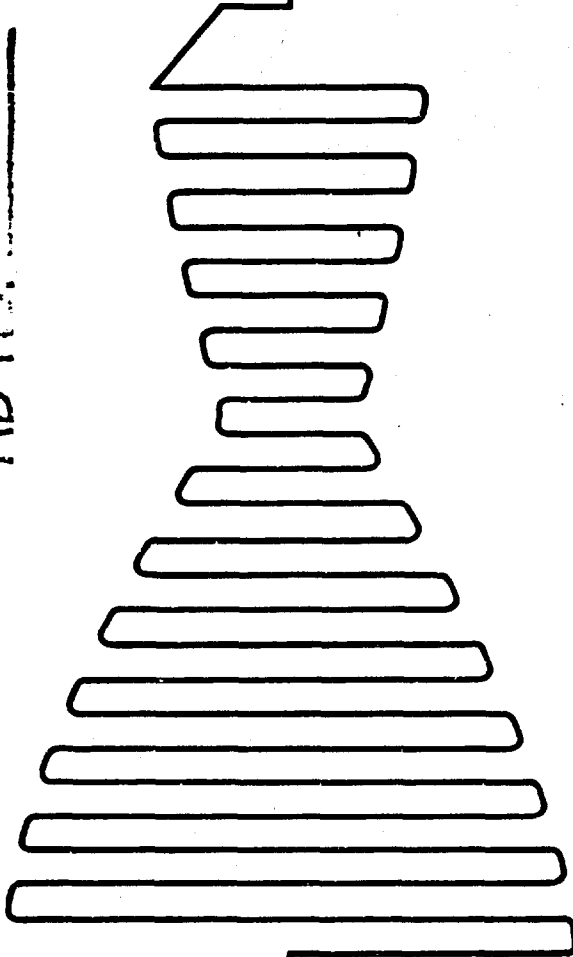
NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Best Available Copy

CONFIDENTIAL

CATALOGED BY ASTIA
AS AD No. _____

324219



ROCKETDYNE
A DIVISION OF NORTH AMERICAN AVIATION, INC.

This material contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794, the transmission or revelation of which in any manner to an unauthorized person is prohibited by law.

DOWNGRADED AT 3 YEAR INTERVALS;
DECLASSIFIED AFTER 18 YEARS
DOD DIR 5200.10

CONFIDENTIAL

CONFIDENTIAL

R-334-15

44

(Unclassified Title)

RESEARCH IN FLUORINE PROPELLANTS
QUARTERLY PROGRESS REPORT
FOR PERIOD ENDING 15 JUNE 1961

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION, INC.

6633 CANOGA AVENUE
CANOGA PARK, CALIFORNIA

Contract Nonr 1818(00)
G. O. 9243

PREPARED BY

E. A. Lawton, H. H. Rogers, J. Q. Weber

APPROVED BY

R. J. Thompson ASL

R. J. Thompson
Director, Research
REVISIONS

NO. OF PAGES 19 & v

ASTIA

JUL 20 1961

INDEX

DATE 15 July 1961

DATE	REV. BY	PAGES AFFECTED	REMARKS

CONFIDENTIAL

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION, INC.

CONFIDENTIAL

Reproduction in whole or in part by the
United States Government is permitted.

R-334-15

CONFIDENTIAL

ii

CONFIDENTIAL

FOREWORD

The research effort described in this report was conducted by the Chemical Synthesis Unit of Rocketdyne's Research Department under Contract Nonr 1818(00) for the period 16 March 1961 through 15 June 1961.

The responsible scientist for this work was Dr. Emil A Lawton and full time associates were Dr. Howard H. Rogers and John Q. Weber.

R-334-15

CONFIDENTIAL

iii

CONFIDENTIAL

ABSTRACT

The electrolysis of solutions of N_2O_4 or other nitrogen-oxygen compounds in anhydrous HF was initiated as a means of synthesizing N-O-F compounds. The reaction of N_2O_4 with HF was investigated and preliminary electrolyses were performed to obtain cell design data. Gas evolution was observed at the anode but not at the cathode, indicating that NO may be a cathodic product. Platinum was found to reduce the voltage necessary to conduct the electrolysis as compared to nickel. Other data necessary for the cell design were determined and the design of the cell and associated equipment is complete.

Difluorourea was reacted with N,N difluorocarbamyl chloride, acetylchloride, perchloryl fluoride, nitrosyl fluoride, and nitryl fluoride under a variety of conditions; but at best, only intractable tars of low oxidizer content were obtained. No new products of interest were obtained by the reaction of N_2F_4 with t-butyl peroxide or with ozone. Ozone did not react with NF_3 or either isomer of N_2F_2 .

(Confidential Abstract)

R-334-15

CONFIDENTIAL

iv

CONFIDENTIAL

CONTENTS

Foreword	iii
Abstract	iv
Introduction	1
Discussion	2
Electrochemistry	2
Reactions of Difluorourea	11
Reactions of Tetrafluorohydrazine	12
Reactions With Ozone	13
Experimental Details	14
Reaction of HF and N_2O_4	14
Electrolysis Equipment and Procedures	14
Electrolysis of Commercial HF	15
Electrolysis of HF- N_2O_4	16
Corrosion Tests	17
Summary and Future Work	18
References	19

R-334-15

CONFIDENTIAL

CONFIDENTIAL

INTRODUCTION

As previously reported on this research program, the development of direct fluorination techniques has resulted in the preparation of several new compounds containing the nitrogen-to-fluorine bond. These were of interest as potential high-energy oxidizers or as intermediates. Subsequently, the use of the electrical discharge also resulted in the formation of other new oxidizer molecules. In this report, the initiation of still another approach towards the synthesis of oxidizers using electrolysis is described. Further, other reactions with difluorourea are also described.

R-334-15

CONFIDENTIAL

CONFIDENTIAL

DISCUSSION

ELECTROCHEMISTRY

The electrochemical approach in oxidizing solutions for the preparation of oxidizers containing nitrogen, oxygen, and fluorine has been selected because it offers interesting preparative possibilities for new compounds. Incidentally, should such compounds be of interest, the method is adaptable to "scaling up."

Much work has been done in the electrolysis of ammonia, amines, pyridine and other nitrogen containing organic compounds dissolved in anhydrous hydrogen fluoride. For example, some N_2F_4 was produced with guanidine in a Simons cell at 0 C and at -7 C, but not at higher temperatures (Ref. 1). Tetranitromethane has been electrolyzed (Ref. 2 and 3) in a Simons Cell, and in a divided cell with KHF_2 as a conductivity additive to yield OF_2 and CF_4 , with minor amounts of NF_3 , C_2F_6 , and NO_2 . Hydrogen evolution was noted in some cases and not in others, apparently depending, at least in part, upon the concentration of tetranitromethane. The electrolysis of an inorganic compound containing the N-O bond was reported by Dow (Ref. 1 and 4). Hydroxylamine dissolved in HF in a Simons Cell yielded no NF_2OF , OF_2 , FNO , or NF_3 , and the analysis of products was complicated by numerous explosions.

The probability of synthesizing relatively unstable N-O-F compounds by electrolysis would be expected to be increased by the low temperatures of operation which will be used in this work. The elimination of organic compounds, precluding the formation of stable CF_4 , should also materially

CONFIDENTIAL

CONFIDENTIAL

increase the possibility of forming these compounds. The work should also be aided by the presence of nitrogen-oxygen compounds where the nitrogen is already in +2, +3, +4, or +5 valence state; this is compared to the nitrogen-hydrogen compounds where the nitrogen formally shows negative valence. In addition, the probability of terminating the reaction prematurely with a stable intermediate such as nitrogen, is lessened. Finally, chances of explosion both in the cell and in the traps is reduced because readily oxidizable materials will be absent.

The need for milder operating conditions was indicated by Kyryacos (Ref. 5). He suggested that fragmentation difficulties could be reduced during the electrochemical fluorination of 1, 2- and 1,3-propanediamine in a Simons Cell if the cell could be operated at less than 5.0 volts. He could not, however, find a measurable rate of fluorination below this voltage. A definite effort will be made at Rocketdyne to keep the operating conditions mild, thereby increasing the chances of synthesizing relatively unstable oxidizers.

The freezing points of N_2O_4 -HF solutions (10 to 60 percent HF) have been investigated (Ref. 5), and a large negative deviation from Raoult's Law observed. Mixtures of N_2O_4 and HF have been used for nitration (Ref. 6). According to Darmois (Ref. 7), nitric acid dissolved in HF dissociates to NO_3^- and a proton trapped between HF molecules. Fredenhagen (Ref. 8) reported that the addition of KNO_2 to anhydrous HF is accompanied by the evolution of nitrous gases and the formation of a colorless solution. However, solutions of KNO_2 in HF give a violet coloration when NO is added (Ref. 9), the color being attributed to the formation of $N_2O_2^+$ ion from NO^+HF . Similar results were also obtained when N_2O_4 , N_2O_3 , and NOF were substituted for KNO_2 .

CONFIDENTIAL

The first experiments were done at Rocketdyne with N_2O_4 , but NO , NOF , N_2O , N_2O_3 , and HNO_3 are also of interest. The electrolysis of these compounds in hydrogen fluoride solution could be expected to present certain corrosion difficulties not normally encountered in the electrolysis of fluorides, because of the presence of strong nitrogen oxidizers. Therefore knowledge of metallic corrosion, under nonelectrolytic as well as anodic and cathodic conditions, was considered necessary. In addition, because N_2O_4 could be expected to behave differently than those compounds previously electrolyzed in HF solution, some insight into the $HF-N_2O_4$ system and into the behavior of electrodes in such a system was also considered necessary. Therefore to maximize the probability of success and to avoid false starts if possible, it was decided to start the research program with a preliminary investigation to obtain the above data. Experiments were conducted to obtain only sufficient data to reach the above objectives; therefore, a thorough interpretive analysis is not considered warranted.

Reaction of HF With N_2O_4

The addition of N_2O_4 to HF to form a colorless solution (Mole ratio $HF:N_2O_4 = 14:1$) is accompanied by hissing and the copious evolution of fumes. The large freezing point depression (Ref. 10) in this system is further evidence of a reaction.

It is interesting to note that in destroying these solutions by the dropwise addition of water, very little evolution of white fumes (from HF), but copious evolution of brown fumes, occurs. Apparently the water displaces the N_2O_4 from the products of the $HF-N_2O_4$ reaction. During this

CONFIDENTIAL

CONFIDENTIAL

work, a green color formed in the solution and the conditions of formation were investigated. The addition of 0.083 moles of ice to a cold solution of 0.036 moles of N_2O_4 in 0.52 moles of HF caused the evolution of brown fumes and the formation of a blue color (probably N_2O_3) near the ice, but the solution stayed colorless after mixing. The further addition of 0.056 moles of ice caused a green color to appear which darkened upon the addition of more ice. This color faded very slowly over a period of several hours with the evolution of brown fumes. The conditions of formation did not appear to be critical and the green color was produced by several other ratios of HF, N_2O_4 , and H_2O , and by HF, $NaNO_2$ and H_2O . No reference to the formation of a green color in HF has been found, although a violet HF, attributed to the formation of a postulated $N_2O_2^+$ ion, has been reported (Ref. 9).

Current-Voltage Relationships of the Electrolytic Cell

The cell current was measured as a function of the composition of the HF- N_2O_4 solution. The objective of these experiments was primarily to find the composition or compositions at which the current was at a maximum, for a constant applied voltage.

The apparatus described under Electrolysis Procedure I, page 15, was used with nickel electrodes. Current peaks (Fig. 1) were obtained for HF- N_2O_4 at mole ratios (HF: N_2O_4) of 400:1 and 36:1. The first is thought to be a result of interaction of impurities in the HF, and the second, a result of the ionization reaction of N_2O_4 . The decrease in current after the second peak is very slow and is probably a dilution effect caused by excess N_2O_4 .

CONFIDENTIAL

CONFIDENTIAL

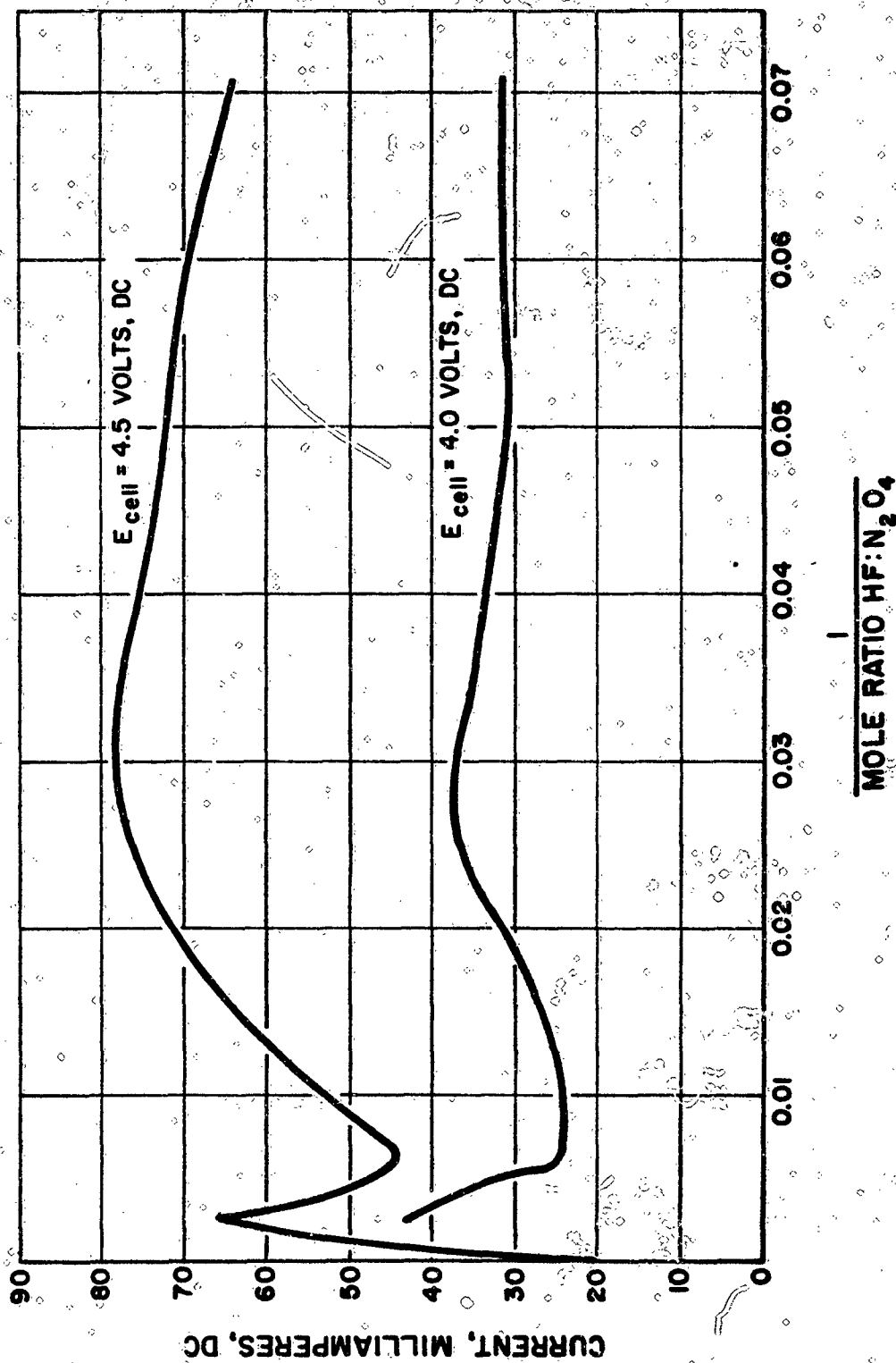


Figure 1. Cell Conductance, DC, for HF-N₂O₄ Using Nickel Electrodes

CONFIDENTIAL

Thermodynamic calculations based on the free energies of reaction in this electrolysis have indicated that NO, rather than hydrogen, is by far the most likely cathodic product of the electrolysis of HF-N₂O₄ solutions. The evolution of hydrogen in some experiments, but not others, in the electrolysis (Ref. 2 and 3) of tetranitromethane solution in HF presents a somewhat similar situation. This may have been a result (in certain experiments) of the formation of NO, which remained in solution, instead of the formation of hydrogen.

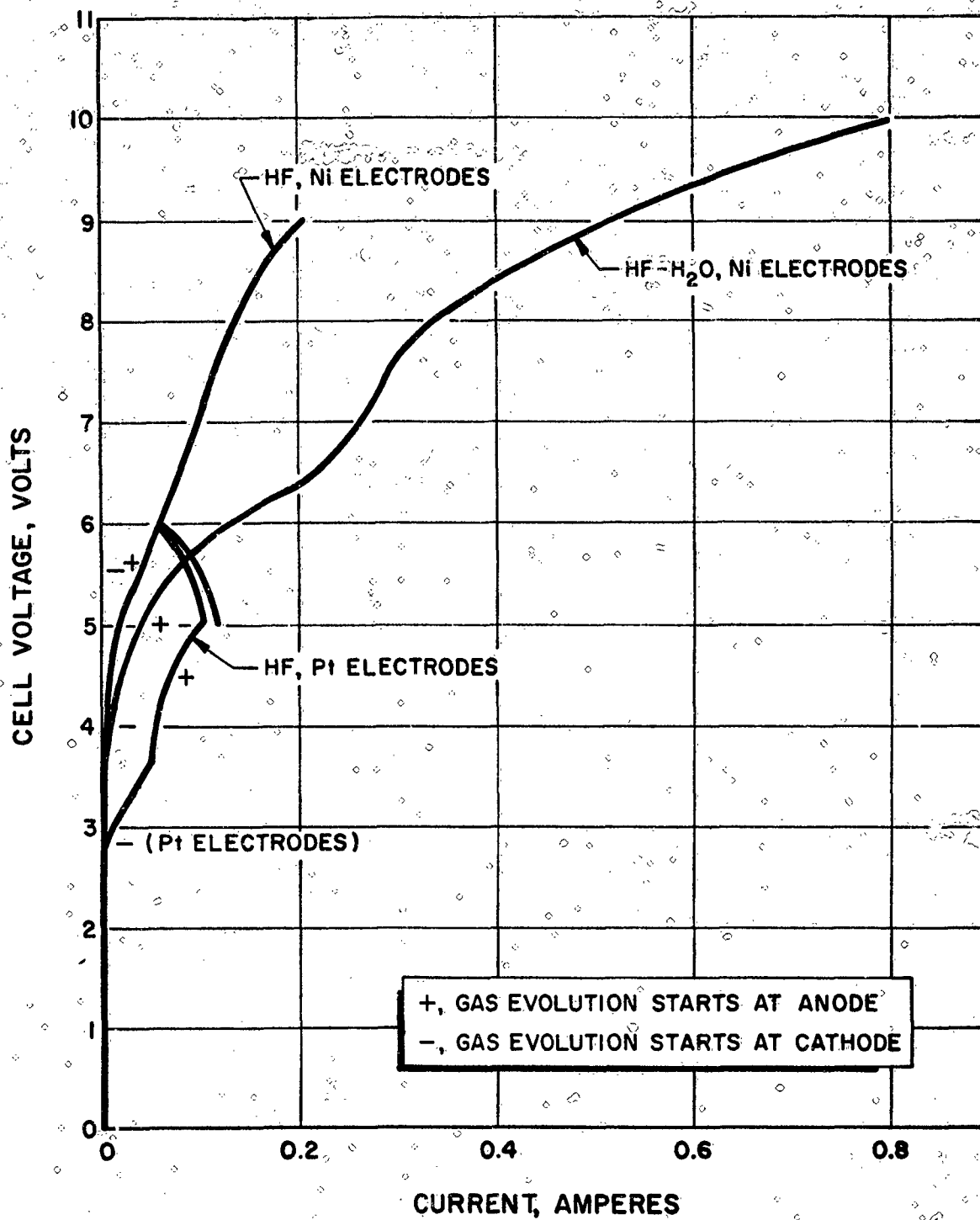
Electrolysis of HF-N₂O₄ Solutions

Numerous experiments were performed to determine the optimum conditions for the electrolysis of HF-N₂O₄ solutions. It was felt that the best cell design could be determined after some of the characteristics of the electrolysis were known. Current and voltage readings were taken with various electrode assemblies. With the experimental arrangements used, cooling was inadequate and considerable increase in cell current with time was noted. At this point in the work, more carefully controlled experiments did not appear to be justified.

Data (Fig. 2) from the electrolysis of HF compared with that obtained from the electrolysis of HF-H₂O indicate that water, a usual impurity in HF, may be responsible for the break in the HF curve at 3.6 volts. The HF-N₂O₄ system shows a similar break at 2.4 volts. It is highly significant that in this system, gas evolution was seen only at the anode, which is consistent with the free energy calculation discussed above. The electrolysis of HF with platinum electrodes was included (Fig. 2) for comparative purposes. The portion of the curve that has a negative slope was correlated with an observed rapid attack of the anode.

CONFIDENTIAL

CONFIDENTIAL

Figure 2. Electrolysis of HF and HF-H₂O (Mole Ratio 17:1)

CONFIDENTIAL

CONFIDENTIAL

In electrolysis work, considerable importance is usually attached to reducing cell potential to prevent decomposition. As can be seen in Fig. 3, the use of another electrode material, such as platinum, will result in milder operating conditions by permitting lower voltages to be used. On the other hand, should more severe conditions be desired, then monel, which requires higher voltages than nickel, could be used as the anode.

Other metals were also examined as electrodes. Type 321 stainless steel, Hastelloy C, iron, Inco A, palladium and cobalt are not satisfactory as anodes. Although the first two alloys are suitable as cathodes, monel is also suitable as a cathode. Both lead and tantalum are attacked rapidly without the application of current.

Cell Design

The cell and associated gas handling and vacuum equipment were designed on the basis of the experimental data. The cell is being made relatively long and thin so that a maximum surface-to-volume ratio is obtained for the most efficient cooling. No gas separation system is needed because gas is evolved from the anode only. It will be possible to add a diaphragm later, if desired, to decrease electrolyte mixing rates.

The cell body is being made from stainless steel because it apparently becomes covered with an insulating film and therefore will not provide an alternate current path if a diaphragm is used. Anodic materials considered at the present time are platinum, nickel and monel. It is important that the anode area be equal to, or greater than the cathode area for maximum cell conductivity. In this design using sheet metal electrodes, the anode and cathode areas will be equal.

CONFIDENTIAL

CONFIDENTIAL

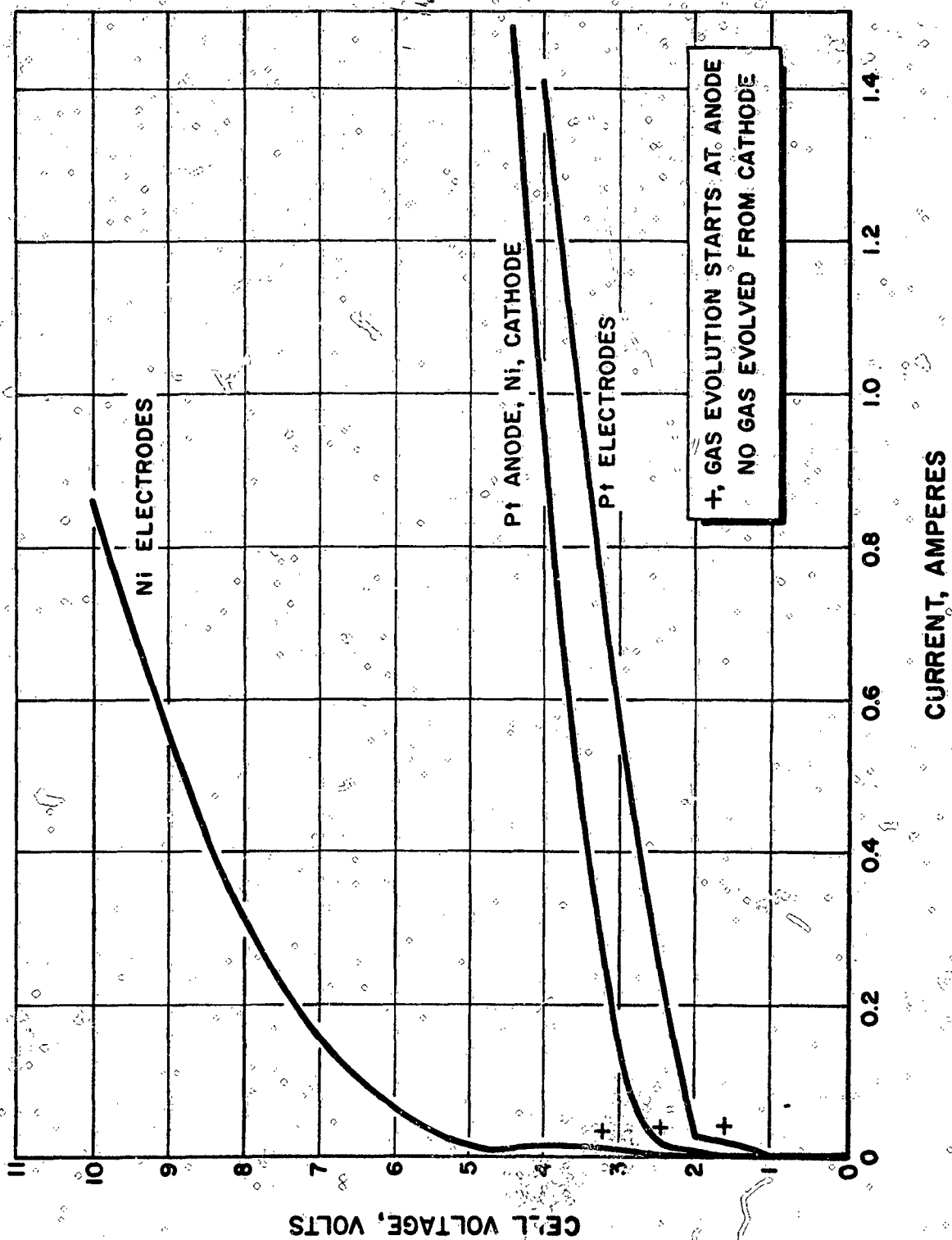
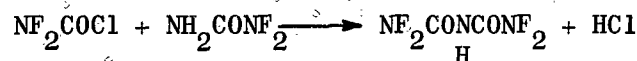


Figure 3. Electrolysis of HF-N₂O₄ (Mole Ratio 36:1)

CONFIDENTIAL

REACTIONS OF DIFLUOROUREA

The availability of difluorourea suggested its use as an intermediate in the preparation of solid NF oxidizers. Since amides are readily acylated, the reactions with acid halides were investigated. Considerable effort was spent to demonstrate whether difluorourea would react with difluorocarbonyl chloride as follows:



The desired tetrafluorobiuret should be a strong acid capable of forming salts and would possibly be a good chelating agent.

The reaction of solid difluorourea with gaseous NF_2COCl proceeded slowly with the conversion of most of the acid chloride to chlorodifluoramine and the formation of a small amount of NH_4F from the NH_2CONF_2 . When ether was used as solvent, no reaction occurred, and, when pyridine was added to the ether solution, intractable tars, with little oxidizing power, resulted.

To determine if difluorourea could be acylated, further experiments were conducted using acetyl chloride in place of the unstable NF_2COCl , since acetyl chloride acetylates urea. Difluorourea did not react with acetyl chloride, either alone or in ether. When pyridine was added, tars which could not be crystallized or sublimed and which had lost their oxidizing power, were again produced.

Similar results were obtained in attempts to react difluorourea with perchloryl fluoride, perchloryl fluoride and pyridine, nitrosyl fluoride and nitryl fluoride. It was concluded that difluorourea is very resistant

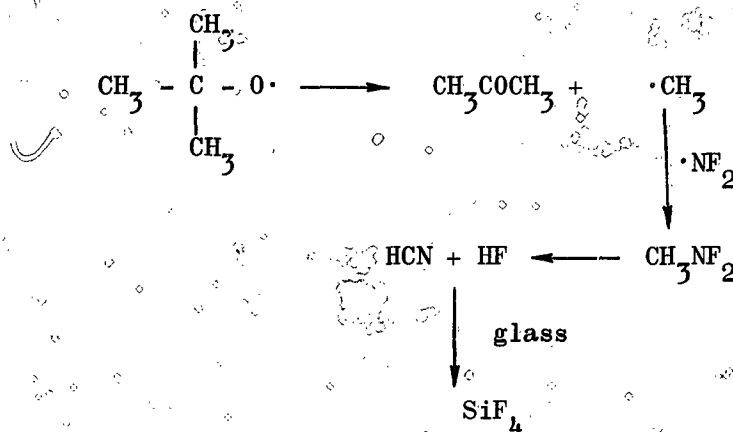
CONFIDENTIAL

CONFIDENTIAL

to direct substitution by acid halides, and although some of the desired types of products may have been formed in the presence of pyridine, side reactions predominated to give intractable mixtures.

REACTIONS OF TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine has been reacted with many compounds using t-butyl peroxide as a catalyst (Ref. 11). Experimental work was performed to determine whether there is a primary reaction between these two materials to form tert-butoxydifluoramine, t-Bu-ONF₂, which might pyrolyze readily to form HONF₂. When N₂F₄ and the peroxide were heated at 140 C, the products were acetone, N₂O, SiF₄, methyldifluoramine, tert-butyldifluoramine and HCN (probably from CH₃NF₂). Irradiation at room temperature with an H-6 ultraviolet source gave a similar mixture (except for alkyldifluoramines), and irradiation at -80 C produced only a trace of HCN. Thus, the t-butoxy radical decomposed to methyl radical, acetone and t-butyl radical, and did not react with NF₂ radical. The products obtained are presumed to have been formed according to the following scheme.



CONFIDENTIAL

CONFIDENTIAL

It was subsequently noted that the thermal reaction between t-butyl peroxide and N_2F_4 was attempted by workers at the General Electric Company (Ref. 12). They obtained formic acid and nitrogen tetroxide but none of the desired compound.

REACTIONS WITH OZONE

It was thought that the highly reactive ozone might react with binary NF compounds to form such substances as NF_3O from NF_3 or NF_2ONF_2 from N_2F_4 . It was also hoped that difluorodiazine might display an unsaturated character toward ozone. However, NF_3 , symmetrical N_2F_2 and unsymmetrical N_2F_2 did not react with ozonized oxygen. Irradiation with soft ultraviolet merely decomposed the ozone, and had no effect on the NF compounds. Tetrafluorohydrazine behaved with ozonized oxygen as it does with ordinary air. There was no reaction until 25 minutes had elapsed; then the contents of the reaction vessel suddenly turned brown.

The N_2F_2 isomers used in this experiment were obtained directly from fluorinated urea liquid and potassium fluoride. The gaseous product from the reaction was almost pure, containing only nitrogen and a trace of N_2O .

CONFIDENTIAL

CONFIDENTIAL

EXPERIMENTAL DETAILS

REACTION OF HF AND N_2O_4

Nitrogen tetroxide (2.5 ml; 40 m moles) was poured slowly into HF (4.2 ml; 210 m moles, Matheson) contained in a semitransparent Kel-F tube. All reagents and containers were cooled in ice before use. The N_2O_4 dissolved with the formation of a lemon-yellow solution, accompanied by violent hissing and initial evolution of fumes. The vapor space above the solution was colored light brown.

When N_2O_4 (0.5 ml; 8 m moles) was added to HF (24.5 ml; 1210 m moles) in another experiment, the addition was accompanied by violent hissing. However, no hissing was noted upon the addition of more N_2O_4 .

ELECTROLYSIS EQUIPMENT AND PROCEDURES

Power was supplied by a continuously variable, unfiltered, full wave rectified supply and measured by calibrated panel meters. A filtered power supply originally ordered for this work, Knight 87FX505, was substituted for the unfiltered supply. No significant difference could be found in the electrolysis of $HF-N_2O_4$, even though the ripple factor was reduced from 47 percent to a maximum of 1.3 percent.

Three different apparatus configurations were used. In each configuration, the electrodes were inserted into the open vessels from above.

CONFIDENTIAL

CONFIDENTIAL

The N_2O_4 was poured slowly into the HF^* . All vessels, graduated cylinders, and reagents were cooled with ice before using and the mixed solution was cooled for a few minutes before electrolyzing.

Electrolysis Procedure I

A translucent Kel-F beaker, 37 mm ID, 65 mm deep, with 5 mm walls was used. The strip electrodes **, 7 mm in width, were immersed to a depth of about 18 mm in the solution and were spaced 13 mm apart. The beaker was immersed in an ice bath over the solution level during electrolysis.

Electrolysis Procedure II

A transparent *** Kel-F beaker, 26 mm ID, 35 mm deep with 3.2 mm walls was used with 10 x 10 mm sheet metal electrodes. The electrodes were fully immersed into the solution, and connected by an extension of the same metal, 1 to 2 mm wide. Spacing was 10 mm.

ELECTROLYSIS OF COMMERCIAL HF

The electrolysis of liquid HF (Matheson) was conducted with nickel electrodes and with platinum electrodes, using Electrolysis Procedure II. The data (Fig. 2) also include that from the electrolysis of $HF-H_2O$, (Mole ratio 17:1) under the same conditions.

* No attempt was made to compensate for the loss of HF or N_2O_4 by vaporization.

** If strip electrodes were unavailable, then rods were used in such a way that an equivalent area was exposed.

*** The use of a transparent Kel-F beaker permitted the visual observation of the electrolysis and thereby, the initiation of gas evolution.

CONFIDENTIAL

CONFIDENTIAL

ELECTROLYSIS OF $\text{HF-N}_2\text{O}_4$

Electrolysis of $\text{HF-N}_2\text{O}_4$ solutions, in the mole ratio of 18:1, using Electrolysis Procedure II with nickel electrodes, is shown in Fig. 3. The substitution of platinum for the nickel cathode had little effect. However, the substitution of a platinum anode caused a significant increase in current density at a given applied voltage. The use of platinum for both the anode and cathode electrodes (Fig. 3) resulted in an almost identical curve and an additional increase in cell current at a given applied voltage.

The data from an experiment using a palladium anode with a nickel cathode shows a sharp break in the curve at 1.7 volts and 6 milliamperes; however gas evolution did not start until the current delivered was 150 milliamperes at 2.0 volts. The remainder of the curve was similar to, but underneath the platinum curves. As might be expected from the delayed start of gas evolution, attack on the palladium was very severe.

Dissolution of both nickel and platinum were also noted, reaching 3 to 10 percent based on the current passed, and assuming a valence change of two for nickel and four for platinum.

Electrolysis - Area Effects

One nickel electrode, 19.5 mm wide and one nickel electrode, 3.0 mm wide, were used alternately as anode and cathode (Electrolysis Procedure I). Significantly higher currents were measured when the larger electrode was used as the anode. For example, at 7.0 volts, 190 milliamperes were measured with the narrow anode, and 530 milliamperes with the wide anode. With two wide electrodes, the curve was almost identical to that obtained with the wide anode and narrow cathode.

CONFIDENTIAL

CORROSION TESTS

Several metals were tested for corrosion resistance in a solution of N_2O_4 (3.9 ml; 62 m moles) in HF (47 ml; 2320 m moles). These were nickel, monel, Hastelloy C, Inco A, and Type 321 stainless steel. The metal strips and rods were mounted in Teflon to prevent electrical contact, then placed in a Kel-F tube and permitted to stand for 17 hours at about 18 C. The tube was stoppered but no other attempt was made to exclude moisture. The amount of corrosion, as determined by weight loss, was negligible.

CONFIDENTIAL

CONFIDENTIAL

SUMMARY AND FUTURE WORK

Investigations of the $\text{HF-N}_2\text{O}_4$ system have led to a suitable electrolytic cell design which is now under construction. A gas handling vacuum system composed of fluorocarbon polymers and metal has been designed and parts ordered.

Investigations of the $\text{HF-N}_2\text{O}_4$ system will continue. It is planned to determine the characteristics of copper, gold, manganese and chromium as anodes. In addition, the ac conductance of the system will be determined as a function of percent N_2O_4 . Further work will also be done with dc current-voltage curves at several specific N_2O_4 concentrations.

The substitution of other solutes for N_2O_4 is also being considered, although it is planned to start electrolysis of $\text{HF-N}_2\text{O}_4$ as soon as the cell and associated equipment are ready.

Further study of the reactions of difluorourea have shown no promising chemistry. Reactions with active halogen compounds did not yield substitution products on the N-H nitrogen as hoped. Reactions of various nitrogen-fluorine compounds with ozone gave no new products.

CONFIDENTIAL

CONFIDENTIAL

REFERENCES

1. AR-3Q-59, Advanced Research on Solid Rocket Propellants, Dow Chemical Co., Midland, Michigan, 28 Aug., 1959 CONFIDENTIAL.
2. Lapkin, M. and M. M. Boudakian, OMCC-5901-TQR-1, Storable High Performance Liquid Bipropellant Systems, Olin Mathieson Chemical Corp., Energy Division, New Haven, Conn., Feb. 1960 CONFIDENTIAL.
3. Lapkin, M. and M. M. Boudakian, OMCC-5901-TQR-2, Storable High Performance Liquid Bipropellant Systems, Olin Mathieson Chemical Corp., Energy Division, New Haven, Conn., May, 1960 CONFIDENTIAL.
4. AR-4Q-59, Advanced Research on Solid Rocket Propellants, Dow Chemical Co., Midland, Michigan, 30 January 1961 CONFIDENTIAL.
5. Kyriacos, G., Moshonas, M. G. and Tsoukalas, S. N. Research on Selective Fluorination Techniques, Report No. 61-7, Penninsular ChemResearch, Inc., Gainesville, Florida, 31 January 1961 CONFIDENTIAL.
6. Clark, I. T. and M. A. Millet, Nitration of Cellulose in Anhydrous Mixtures of N_2O_4 and HF, TAPPI 44, 144-6 (1961).
7. Darmois, G., Conductivity and Associated Properties of Liquid HF, J. chim. phys. 53, 445-50 (1956); C.A. 50, 13569 (1956).
8. Fredenhagen, H., Precipitation Reactions and Double Decompositions in Liquid Hydrogen Fluoride, Z. anorg. allgem. Chem. 242, 31 (1939).
9. Seel, F. and H. Sauer, Violet Hydrofluoric Acid, Angew. Chem. 69, 135 (1957); C.A. 52, 1828 (1958).
10. AL-1477, Missile and Control Equipment, 2.75 Inch Liquid-Propellant Aircraft Rocket (NALAR), Phase V Summary Report, North American Aviation, Inc., Downey, Calif., 26 June 1952 CONFIDENTIAL.
11. P 59-14, Quarterly Progress Report on Propellant Research, 1 May-31 July 1959, Rohm and Haas Co., Huntsville, Alabama, 12 November 1959 CONFIDENTIAL.
12. Storable Liquid Propellant Systems--Storable Oxidizers, Final Report, Vol. 2, 1 July 1959 - 28 February 1961; General Electric Company, Cincinnati, Ohio CONFIDENTIAL.

CONFIDENTIAL